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December 9, 1997

**BOX PATENT APPLICATION**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Re: Application of Masao INOUE, Masao OGAWA and Hiroshi NAKAMURA  
"GRANULAR PESTICIDAL COMPOSITION"  
Our Ref: Q48500

Dear Sir:

Attached hereto is the application identified above including 41 sheets of the specification and claims and a Preliminary Amendment. **The executed Declaration and Power of Attorney and Assignment will be submitted at a later date.**

The Government filing fee is calculated, after entry of the Preliminary Amendment, as follows:

Total claims	$\frac{28}{2} - 20 = \underline{\quad} \times \$22 =$	\$ 176.00
Independent claims	$\underline{2} - 3 = \underline{\quad} \times \$82 =$	\$
Base Fee		\$ 790.00
Multiple Dependent Claim Fee		\$ <u>270.00</u>
<b>TOTAL FILING FEE</b>		<b>\$1236.00</b>

A check for the statutory filing fee of \$1236.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16 and 1.17 and any petitions for extension of time under 37 C.F.R. § 1.136 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from December 11, 1996 based on Japanese Patent Application No. 330699/96. A certified copy of the priority document is enclosed herewith.

Respectfully submitted,

SUGHRUE, MION, ZINN,  
MACPEAK & SEAS, PLLC  
Attorneys for Applicant

By: J. Frank Osha  
J. Frank Osha  
Reg. No. 24,625

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

INOUE et al.

Application No.:

Group Art Unit:

Filed: December 9, 1997

Examiner:

For: GRANULAR PESTICIDAL COMPOSITION

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-referenced application,  
kindly enter the following amendments to the claims.

IN THE CLAIMS:

Claim 3, line 2, delete "or 2".

Claim 4, line 2, delete "or 3".

Claim 5, lines 1-2, delete "any one of claims 1 to 4" and  
insert --claim 1--.

Claim 6, line 2 after "5", insert --or 7 to 15--.

Please add the following new claims:

--7. The granular pesticidal composition according to Claim 2,  
wherein the proportion of the thermosetting resin is from 0.5 to 15  
parts by weight based on 100 parts by weight of a pesticidal active  
ingredient-containing granule to be coated.

8. A granular pesticidal composition according to claim 3,  
wherein the thermosetting resin is prepared from polyisocyanate

having tri- or higher isocyanate groups and/or polyole having tri- or higher hydroxy groups.

9. A granular pesticidal composition according to claim 7, wherein the thermosetting resin is prepared from polyisocyanate having tri- or higher isocyanate groups and/or polyole having tri- or higher hydroxy groups.

10. A granular pesticidal composition according to claim 2, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

11. A granular pesticidal composition according to claim 3, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

12. A granular pesticidal composition according to claim 4, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

13. A granular pesticidal composition according to claim 7, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

14. A granular pesticidal composition according to claim 8, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

15. A granular pesticidal composition according to claim 9, wherein the water absorption ratio of the thermosetting resin is not more than 5%.--

INOUE et al.  
Q48500  
Information Disclosure Statement

REMARKS

Claims 1-6 have been amended and new claims 7-15 have been amended to correct the improper multiple dependency of the claims. No new matter has been added.

Respectfully submitted,



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J. Frank Osha  
Reg. No. 24,625

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Date: December 9, 1997

## Granular Pesticidal Composition

The present invention relates to a granular pesticidal composition in which release of a pesticidal active  
5 ingredient therein is restrained.

The present invention has been made to give controlled release of the pesticidal active ingredient, and provides a granular pesticidal composition endowed with effect of restraining release of a pesticidal active ingredient from  
10 the granular pesticidal composition and sustained efficacy of the pesticidal active ingredient.

The present invention relates to a granular pesticidal composition coated with a thermosetting resin. Also, the present invention relates to the granular pesticidal  
15 composition in which the thermosetting resin is a polyurethane resin, and the granular pesticidal composition in which the proportion of the thermosetting resin is from 0.5 to 15 parts by weight based on 100 parts by weight of the pesticidal active ingredient-containing granule to be  
20 coated.

Conventionally, a method is known for formulating pesticidal granules using a resin component as a binder (Japanese Patent Application Laid-Open (JP-A) No. 58-205536).

25 In the present invention, the pesticidal active ingredient-containing granule to be coated with the

thermosetting resin is obtained by making a pesticidally active ingredient to be supported with carrier which is usually used for formulation of a pesticidal active ingredient.

5       The examples of the pesticidal active ingredient include the following compounds.

(1)  $\alpha$ -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate

(2) (S)- $\alpha$ -cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-  
10 3-methylbutyrate

(3)  $\alpha$ -cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate

(4) 3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

15 (5) 3-phenoxybenzyl chrysanthemate

(6) 3-phenoxybenzyl (1R)-chrysanthemate

(7)  $\alpha$ -cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

(8)  $\alpha$ -cyano-3-(4-chlorophenoxy)benzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate  
20

(9)  $\alpha$ -cyano-3-(4-fluorophenoxy)benzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

(10)  $\alpha$ -cyano-3-phenoxybenzyl chrysanthemate

(11)  $\alpha$ -cyano-3-phenoxybenzyl (1R)-chrysanthemate

25 (12)  $\alpha$ -cyano-3-(4-chlorophenoxy)benzyl 2-(4-chlorophenyl)-3-methylbutyrate

- (13)  $\alpha$ -cyano-3-(4-fluorophenoxy)benzyl 2-(4-chlorophenyl)-3-methylbutyrate
- (14)  $\alpha$ -cyano-3-phenoxybenzyl 2-(4-tert-butylphenyl)-3-methylbutyrate
- 5 (15)  $\alpha$ -cyano-3-phenoxybenzyl 2-(3,4-methylenedioxyphenyl)-3-methylbutyrate  
[0008]
- (16)  $\alpha$ -cyano-4-fluoro-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
- 10 (17)  $\alpha$ -cyano-3-phenoxybenzyl 2-(2-chloro-4-trifluoromethylanilino)-3-methylbutyrate
- (18)  $\alpha$ -cyano-3-phenoxybenzyl 2-(4-difluoromethoxyphenyl)-3-methylbutyrate
- (19)  $\alpha$ -cyano-3-phenoxybenzyl (S)-2-(4-difluoromethoxyphenyl)-3-methylbutyrate
- 15 (20) cyano-(5-phenoxy-2-pyridyl)methyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
- (21)  $\alpha$ -cyano-3-phenoxybenzyl 2,2-dimethyl-3-(1,2,2,2-tetrabromoethyl)cyclopropanecarboxylate
- 20 (22)  $\alpha$ -cyano-3-phenoxybenzyl 2,2-dimethyl-3-(1,2-dichloro-2,2-dibromoethyl)cyclopropanecarboxylate
- (23)  $\alpha$ -cyano-3-phenoxybenzyl 1-(4-ethoxyphenyl)-2,2-dichloropropanecarboxylate
- (24)  $\alpha$ -cyano-3-phenoxybenzyl 2,2-dimethyl-3-(2-chloro-2-trifluoromethylvinyl)cyclopropanecarboxylate
- 25 (25) 2-(4-ethoxyphenyl)-2-methylpropyl 3-phenoxybenzyl

ether

(26) 2-(4-ethoxyphenyl)-3,3,3-trifluoropropyl 3-  
phenoxybenzyl ether

(27) 2-methyl-3-phenylbenzyl (1R, trans)-2,2-dimethyl-3-  
5 (2-chloro-2-trifluoromethylvinyl)cyclopropanecarboxylate

(28) 2,3,5,6-tetrafluorobenzyl (1R, trans)-3-(2,2-  
dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

(29) 3,4,5,6-tetrahydrophthalimidemethylchrysanthemate

(30) 3,4,5,6-tetrahydrophthalimidemethyl (1R)-  
10 chrysanthemate

(31) 3-allyl-2-methyl-4-oxocyclopent-2-enyl  
chrysanthemate

(32) 3-allyl-2-methyl-4-oxocyclopent-2-enyl (1R)-  
chrysanthemate

15 (33) (S)-2-methyl-4-oxo-3-(2-propinyl)cyclopent-2-enyl  
(1R)-chrysanthemate

(34) 1-ethynyl-2-methyl-2-pentenyl (1R)-chrysanthemate

(35) 5-benzyl-3-furylmethylchrysanthemate

(36) 5-benzyl-3-furylmethyl (1R)-chrysanthemate

20 (37)  $\alpha$ -cyano-3-phenoxybenzyl 3-(2,2-dibromovinyl)-2,2-  
dimethylcyclopropanecarboxylate

(38) 6-neopentyloxymethyl-2-phenoxy pyridine

(39) O,O-dimethyl O-(3-methyl-4-nitrophenyl)  
phosphorothioate

25 (40) O,O-dimethyl O-(cyanophenyl) phosphorothioate

(41) S- $\alpha$ -ethoxycarbonylbenzyl O,O-dimethyl



phosphorodithioate

(42) O,O-dimethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl)

phosphorothioate

(43) O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl)

5 phosphorothioate

(44) O,O-dimethyl O-[3-methyl-4-(methylthio)phenyl]

phosphorothioate

(45) O-(4-bromo-2,5-dichlorophenyl) O,O-diethyl

phosphorothioate

10 (46) 2-methoxy-4H-1,3,2-benzoxaphosphorine-2-sulfide

(47) O,O-dimethyl O-(2,4,5-trichlorophenyl)

phosphorothioate

(48) O,O-dimethyl O-(3,5,6-trichloro-2-pyridyl)

phosphorothioate

15 (49) O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)

phosphorothioate

(50) O,O-dimethyl O-(4-bromo-2,5-dichlorophenyl)

phosphorothioate

(51) O-(2,4-dichlorophenyl) O-ethyl S-propyl

20 phosphorodithioate

(52) O,O-dimethyl S-(5-methoxy-1,3,4-thiadiazoline-2-on-3-ylmethyl) phosphorodithioate

(53) dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate

(54) O-ethyl O-(4-nitrophenyl) benzenephosphonothioate

25 (55) O,O-dimethyl S-(N-methylcarbamoylmethyl)

phosphorodithioate

- (56) O,O-dimethyl O-[3-methyl-4-(methylsulfinyl)phenyl]  
phosphorothioate
- (57) O-(2,4-dichlorophenyl) O,O-diethyl phosphorothioate
- (58) O-2-diethylamino-6-methylpyrimidine-4-yl O,O-
- 5 dimethyl phosphorothioate
- (59) O,O-diethyl O-(5-phenyl-3-isoxazolyl)  
phosphorothioate
- (60) O,O-diethyl O-(3-oxo-2-phenyl-2H-pyridazin-6-yl)  
phosphorothioate
- 10 (61) S-2-ethylsulfinyl-1-methylethyl O,O-dimethyl  
phosphorothioate
- (62) O,O-dimethyl S-2-(1-methylcarbamoylethylthio)ethyl  
phosphorothioate
- (63) S-2-ethylthioethyl O,O-dimethyl phosphorodithioate
- 15 (64) S-2-isopropylthioethyl O,O-dimethyl  
phosphorodithioate
- (65) 3-diethoxyphosphorylthiomethyl-6-chlorobenzoxazolone
- (66) O,O-dimethyl S-phthalimidemethyl phosphorodithioate
- (67) S-[5-methoxy-1,3,4-thiadiazole-2(3H)-on-3-ylmethyl]
- 20 O,O-dimethyl phosphorodithioate
- (68) 3-dimethoxyphosphinoxyloxy-N-methylisocrotonamide
- (69) 2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl  
phosphate
- (70) 2-chloro-1-(2,4-dichlorophenyl)vinyl dimethyl
- 25 phosphate
- (71) 2-chloro-1-(2,4-dichlorophenyl)vinyl diethyl

phosphate

- (72) O,O-dipropyl O-[4-(methylthio)phenyl] phosphate  
(73) O-(4-cyanophenyl) O-ethyl phenylphosphonothioate  
(74) O-(2,4-dichlorophenyl) O-ethyl phenylphosphonothioate  
5 (75) O-2,6-dichloro-p-tolyl O,O-dimethyl phosphorothioate  
(76) 2-sec-butylphenyl methylcarbamate  
(77) 3-methylphenyl methylcarbamate  
(78) 3,4-dimethylphenyl methylcarbamate  
(79) 3,4-isopropylphenyl methylcarbamate  
10 (80) 2,3-dihydro-2,2-dimethyl-7-benzofuranyl  
(dibutylaminothio) methylcarbamate  
(81) 1-methylethyl (3-chlorophenyl) carbamate  
(82) S-ethyl dipropylthiocarbamate  
(83) 3-[(methoxycarbonyl)amino]phenyl (3-  
15 methylphenyl)carbamate  
(84) S-ethyl azepane-1-carbothioate  
(85) S-4-chlorobenzyl diethylthiocarbamate  
(86) methyl 1-(butylcarbamoyl) benzimidazole-2-ylcarbamate  
(87) S-(1-methyl-1-phenylethyl) 1-piperidinecarbothioate  
20 (88) S-benzyl 1,2-dimethylpropyl (ethyl) thiocarbamate  
(89) O-4-tert-butylphenyl 6-methoxy-2-pyridyl (methyl)  
thiocarbamate  
(90) O-3-tert-butylphenyl 6-methoxy-2-pyridyl (methyl)  
thiocarbamate  
25 (91) O-(4-chloro-3-ethylphenyl) 6-methoxy-2-pyridyl  
(methyl) thiocarbamate

- (92) O-(4-bromo-3-ethylphenyl) 6-methoxy-2-piridyl  
(methyl) thiocarbamate
- (93) O-(4-trifluoromethylphenyl) 6-methoxy-2-piridyl  
(methyl) thiocarbamate
- 5 (94) isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate
- (95) ethyl 2-(4-phenoxyphenoxy) ethylcarbamate
- (96) 2-[1-methyl-2-(4-phenoxyphenoxy)ethoxy]pyridine
- (97) 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea
- 10 (98) 1-[3,5-dichloro-4-(3-chloro-5-trifluoromethyl-2-piridyloxy)phenyl]-3-(2,6-difluorobenzoyl)urea
- (99) 1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea
- (100) 1-[3,5-dichloro-4-(1,1,2,2-
- 15 tetrafluoroethoxy)phenyl]-3-(2,6-difluorobenzoyl)urea
- (101) 1-[4-(2-chloro-4-trifluoromethylphenoxy)-2-fluorophenyl]-3-(2,6-difluorobenzoyl)urea
- (102) trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-3-thiazolidinecarboxamide
- 20 (103) 2-tert-butyl-5-(4-tert-butylbenzylthio)-4-chloropiridazin-3(2H)-one
- (104) tert-butyl (E)- $\alpha$ -(1,3-dimethyl-5-phenoxy-4-ylmethyleneaminoxy)-p-toluate
- (105) 3,7,9,13-tetramethyl-5,11-dioxa-2,8,14-trithia-
- 25 4,7,9,12-tetraazapentadeca-3,12-diene-6,10-dione
- (106) 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidine-

2-ylideneamine

(107) (E)-4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one

(108) (E)-N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-

5 methyl-2-nitrovinylienediamine

(109) 5-ethoxy-3-(trichloromethyl)-1,2,4-thiadiazole

(110) 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)aniline

(111) N-(1,1,3-trimethyl-2-oxa-4-indanyl)-5-chloro-1,3-dimethylpyrazole-4-carboxamide

10 (112) 3'-isopropoxy-2-(trifluoromethyl)benzanilide

(113) 3'-isopropoxy-2-methylbenzanilide

(114) diisopropyl 1,3-dithiolane-2-ylidenemalonate

(115) 1,2,5,6-tetrahydropyrrolo [3,2,1-ij]quinolin-4-one

(116) 3-(2-propenyloxy)-1,2-benzisothiazole 1,1-dioxide

15 (117) 5-methyl-1,2,4-triazolo[3,4-b]benzothiazole

(118) dimethyl 4,4'-(o-phenylene)bis(3-thioallophanate)

(119) 1-(4-chlorobenzyl)-1-cyclopentyl-3-phenylurea

(120) 6-(3,5-dichloro-4-methylphenyl)-3(2H)-pyridazinone

(121) (Z)-2'-methylacetophenone 4,6-dimethylpyrimidine-

20 2-ylhydrazone

(122) 3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide

(123) 3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidin-2,4-dione

25 (124) N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboxyimide

- (125) N-(R)-[1-(4-chlorophenyl)ethyl]-2,2-dichloro-1-ethyl-3-tert-methyl-1-cyclopropanecarboxamide
- (126) isopropyl 3,4-diethoxyphenylcarbamate
- (127) methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl]-3-methoxyacrylate
- 5 (128) N-[1-(2,4-dichlorophenylethyl)]-2-cyano-3,3-dimethylbutaneamide
- (129) manganese ethylenebis (dithiocarbamate)
- (130) ethylenebis(dithiocarbamic acid)manganese and zinc
- 10 (131) N-(trichloromethylthio)cyclohexa-4-ene-1,2-dicarboximide
- (132) tetrachloroisophthalonitrile
- (133) 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-one
- 15 (134) (E)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazole-1-yl)-1-penten-3-ol
- (135) (E)-1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl)-1-pentene-3-ol
- (136) (E)-4-chloro- $\alpha, \alpha, \alpha$ -trifluoro-N-(1-imidazol-1-yl-2-propoxyethylidene)-o-toluidine
- 20 (137) methyl N-(2-methoxyacetyl)-N-(2,6-xylyl)alaninate
- (138) 3-chloro-N-(3-chloro-5-trifluoromethyl-2-pyridyl)-2,6-dinitro-4-methylaniline
- (139) 3',4'-dichloropropioneanilide
- 25 (140) 2-chloro-2',6'-diethyl-N-methoxymethylacetoanilide
- (141) N-butoxymethyl-2-chloro-2',6'-diethylacetoanilide

- (142) 2-chloro-2',6'-dimethyl-N-(3-methoxy-2-thenyl)acetoanilide
- (143) 2-chloro-2',6'-diethyl-N-(2-propoxyethyl)acetoanilide
- 5 (144) N-(2-cis-buteneoxy)methyl-2-chloro-2',6'-diethylacetoanilide
- (145) ethyl N-chloroacetyl-N-(2,6-diethylphenyl)glycinate
- (146) 2-bromo-N-( $\alpha,\alpha$ -dimethylbenzyl)-3,3-dimethylbutaneamide
- 10 (147) 1-(1-methyl-1-phenylethyl)-3-p-tolylurea
- (148) 1-(2-chlorobenzyl)-3-( $\alpha,\alpha$ -dimethylbenzyl)urea
- (149) 3-(4-chlorophenyl)-1,1-dimethylurea
- (150) 3-(3,4-dichlorophenyl)-1,1-dimethylurea
- (151) 2',3'-dichloro-4-ethoxymethoxybenzanilide
- 15 (152) 2-benzothiazol-2-yloxy-N-methylacetoanilide
- (153) 2-(2-naphtyloxy)propioneanilide
- (154) 2-(2,4-dichloro-m-tolyloxy)propioneanilide
- (155) 4-(2,4-dichlorobenzoyl)-1,3-dimethylpirazol-5-yl toluene-4-sulfonate
- 20 (156) 2-[4-(2,4-dichlorobenzoyl)-1,3-dimethylpirazol-5-yloxy]acetophenone
- (157) 2-[4-(2,4-dichloro-3-methylbenzoyl)-1,3-dimethylpirazol-5-yloxy]-p-methylacetophenone
- (158) 2,4,6-trichlorophenyl 4-nitrophenyl ether
- 25 (159) 2,4-dichlorophenyl 3-methoxy-4-nitrophenyl ether
- (160) 2,4-dichlorophenyl 3-methoxycarbonyl-4-nitrophenyl

ether

- (161) 5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-  
1,3,4-oxadiazol-2(3H)-one
- (162) 2-amino-3-chloro-1,4-naphthoquinone
- 5 (163) methyl 2-[3-(4,6-dimethoxypyrimidin-2-  
yl)ureidosulfonyl]benzoate
- (164) 3-(4,6-dimethoxy-1,3,5-triazin-2-yl)-1-[2-(2-  
methoxyethoxy)phenylsulfonyl]urea
- (165) ethyl 5-[3-(4,6-dimethoxypyrimidin-2-  
10 yl)ureidosulfonyl]-1-methylpirazole-4-carboxylate
- (166) 3-chloro-2-[4-chloro-2-fluoro-5-(2-  
propinyloxy)phenyl]-4,5,6,7-tetrahydro-2H-indazole
- (167) N-[4-chloro-2-fluoro-5-(1-methyl-2-  
propinyloxy)phenyl]-3,4,5,6-tetrahydrophthalimide
- 15 (168) N-[4-chloro-2-fluoro-5-  
(pentyloxy-carbonylmethoxy)phenyl]-3,4,5,6-  
tetrahydrophthalimide
- (169) 7-fluoro-6-(3,4,5,6-tetrahydrophthalimide)-4-(2-  
propinyl)-1,4-benzoxazin-3(2H)-one
- 20 (170) 3-chloro-2-[7-fluoro-4-(2-propinyl)-3,4-dihydro-  
1,4-benzoxazin-3(2H)-on-6-yl]-4,5,6,7-tetrahydro-2H-  
indazole
- (171) 1-[2-chloroimidazo[1,2-a]pyridin-3-ylsulfonyl-3-  
(4,6-dimethoxypyrimidinyl)urea
- 25 (172) 3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-on-2,2-  
dioxide



- (173) 2-(1-ethoxyiminobutyl)-5-[2-(ethylthio)propyl]-3-hydroxycyclohexa-2-en-1-one
- (174) 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
- 5 (175) 2-methylthio-4,6-bis(ethylamino)-1,3,5-triazine
- (176) 2-chloro-4,6-bis(ethylamino)-1,3,5-triazine
- (177) 2-methylthio-4-ethylamino-6-(1,2-dimethylpropylamino)-1,3,5-triazine
- (178) 2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one
- 10 (179) 4'-chloro-2'-( $\alpha$ -hydroxybenzyl)isonicotineanilide
- (180) 6-(benzylamino)purine
- (181) 6-(furfurylamino)purine
- (182) 2,4-dinitro-6-sec-butylphenol
- 15 (183) N-[2,4-dimethyl-5-[[ (trifluoromethyl)sulfonyl]amino]phenyl]acetoamide
- (184) 1-(2-chloro-4-pyridyl)-3-phenylurea
- (185) S,S-dimethyl 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)pyridine-3,5-dicarbothioate
- 20 (186) exo-1-methyl-4-(1-methylethyl)-2-(2-methylphenylmethoxy)-7-oxabicyclo[2.2.1]heptane

These pesticidal active ingredients may be used alone or in combination of two or more, and contained in the

25 pesticidal active ingredient-containing granule which is to be coated with the thermosetting resin in an amount usually

from 0.1 to 90% by weight, and preferably from 1 to 80% by weight.

In the present invention, the pesticidal active ingredient-containing granule which is to be coated with the thermosetting resin can be obtained by supporting a pesticidal active ingredient by a solid carrier such as an mineral carrier, vegetable carrier, water-soluble carrier, synthetic carrier or the like, and then, a surfactant, water-soluble polymer, solvent, stabilizer, dye stuff, perfume and the like are optionally added.

The pesticidal active ingredient-containing granule generally contains 1 to 97% by weight of the carrier(s) in addition to 0.1 to 90% by weight of the pesticidal active ingredient, and may further contain 0.1 to 40% by weight, preferably 1 to 20% by weight of the surfactant and/or water-soluble polymer, not more than 30% by weight, preferably 0.1 to 20% by weight of the solvent, 0.01 to 10% by weight of the stabilizer, and 0.01 to 5% by weight of the coloring agent and/or perfume, respectively.

To support the pesticidal active ingredient by the carrier, a conventional production method for a pesticidal granule may be used, and usually a granulator is used such as an extrusion granulator, compression granulator, stirring granulator, fluidized bed granulator and the like, and the granulation is generally conducted to obtain a granule having a diameter from 0.1 to 5 mm, preferably from 0.5 to 3 mm.

The examples of the mineral carrier used to obtain the pesticidal active ingredient-containing granule include kaolin minerals such as kaolinite, dickite, nacrite, halocite and the like, serpentinite such as chrysotile, lizardite, anticolite, amecite and the like, smectite such as calcium montmorillonite, magnesium montmorillonite, saponite, hectorite, sauconite, beidellite and the like, mica such as pyrophyllite, talc, siderite, muscovite, phengite, sericite, illite and the like, silica such as cristobalite, quartz and the like, hydrated magnesium silicate such as atapalgite, sepiolite and the like, calcium carbonate such as dolomite and the like, sulfate minerals such as gypsum and the like, zeolite, tuff, vermiculite, laponite, pumice, diatomite, acidic clay, activated clay and the like.

The examples of the vegetable carrier include cellulose, hull, wheat flour, wood flour, starch, bran, wheat bran, soy bean flour and the like. The examples of the water-soluble carrier include lactose, sucrose, dextrin, sodium chloride, mirabilite, sodium tripolyphosphate, potassium pyrophosphate, sodium hydrogencarbonate, sodium carbonate, potassium carbonate, potassium hydrogencarbonate, maleic acid, citric acid, fumaric acid, malic acid and the like, and the examples of the synthetic carrier include wet silica, dry silica, calcinated product of wet silica, processed starch (ex. Pineflow manufactured by Matsutani Kagaku K.K.)

and the like.

The examples of the surfactant include nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylaryl ether, polyoxyethylenelanolin  
5 alcohol, polyoxyethylenealkylphenol formalin condensate, polyoxyethylenesorbitan fatty acid ester, polyoxyethyleneglyceryl mono fatty acid ester, polyoxypropylene glycol mono fatty acid ester, polyoxyethylene sorbitol fatty acid ester, polyoxyethylene  
10 castor oil derivatives, polyoxyethylene fatty acid ester, higher fatty acid glycerin ester, sorbitan fatty acid ester, sucrose fatty acid ester, polyoxyethylene polyoxypropylene block polymer, polyoxyethylene fatty acid amide, alkylol amide, polyoxyethylenealkylamine and the like; cationic  
15 surfactants such as alkylamine hydrochlorides such as dodecylamine hydrochloride and the like, quaternary alkyl ammonium salts such as dodecyltrimethyl ammonium salt, alkyl dimethylbenzyl ammonium salt, alkylpyridinium salt, alkylisoquinolynium salt, dialkyl morphonium salt and the  
20 like, benzetonium chloride, polyalkylvinyl pyridinium salt and the like; anionic surfactants such as sodium salts of fatty acids such as sodium palmitate and the like, sodium ether carboxylates such as sodium polyoxyethylene lauryl ether carboxylate, amino acid condensate of higher fatty acid  
25 such as sodium lauroylsarcosine, sodium N-lauroyl glutamate and the like, higher fatty acid ester sulfonates such as a

higher alkylsulfonate, lauric acid ester sulfonate and the like, dialkyl sulfosuccinates such as dioctyl sulfosuccinate and the like, higher fatty acid amide sulfonates such as oleic amide sulfonate and the like, alkyl aryl sulfonates such as sodium dodecylbenzene sulfonate, diisopropylnaphthalene sulfonate and the like, formalin condensate of alkyl aryl sulfonate, salt of higher alcohol sulfuric acid ester such as pentadecane-2-sulfate, polyoxyethylene alkylphosphate such as dipolyoxyethylene dodecyl ether phosphate and the like, styrene-maleic acid; ampholytic surfactants such as N-lauryl alanine, N,N,N-trimethylaminopropionic acid, N,N,N-trihydroxyethylaminopropionic acid, N-hexyl-N,N-dimethylaminoacetic acid, 1-(2-carboxyethyl)pyridinium betaine, lecithin and the like.

15       The examples of the water-soluble polymer include gum arabic, sodium carboxymethyl cellulose, hydroxypropylmethyl cellulose, methyl cellulose, methylethyl cellulose, hydroxypropyl cellulose, sodium polyacrylate, tragacanth gum, polyvinylpyrrolidone, alginic acid, sodium alginate, 20 polyoxyethylene having a molecular weight of not less than 6000, modified starch and the like. And the examples of the solvent include saturated aliphatic hydrocarbons such as decane, tridecane, tetradecane, hexadecane, octadecane and the like, unsaturated aliphatic hydrocarbons such as 1- 25 undecene, 1-heneicosene and the like, halogenated hydrocarbons such as Cereclor S45 (solvent manufactured by

ICI) and the like, ketones such as methyl ethyl ketone, cyclohexanone and the like, alcohols such as ethanol, butanol, octanol and the like, esters such as ethyl acetate, dimethyl phthalate, methyl laurate, ethyl palmitate, octyl acetate, 5 dioctyl succinate, didecyl adipate and the like, alkylbenzenes such as xylene, ethylbenzene, octadecylbenzene, Solvesso (solvent manufactured by Exxon Chemical Corp.), Hisol SAS-296 (solvent manufactured by Nisseki Kagaku K.K.) and the like, alkylnaphthalenes such 10 as dodecylnaphthalene, tridecylnaphthalene, Solvesso 200 (solvent manufactured by Exxon Chemical Corp.) and the like, glycols such as ethylene glycol, diethylene glycol, tetraethylene glycol, polypropylene glycol and the like, glycol ethers such as propylene glycol monomethyl ether, 15 ethylene glycol monoethyl ether and the like, fatty acids such as oleic acid, capric acid, enanthic acid and the like, acid amides such as N,N-dimethylformamide, N,N-diethylformamide and the like, animal and vegetable oils such as olive oil, soybean oil, rape seed oil, castor oil, linseed 20 oil, cotton seed oil, palm oil, avocado oil, shark liver oil and the like, mineral oils such as machine oil and the like, glycerine, glycerine derivatives such as glycerine fatty acid ester and the like.

The examples of the stabilizer include antioxidants 25 such as phenol-based antioxidant, amine-based antioxidant, phosphorus-based antioxidant, sulfur-based antioxidant, and

the like, ultraviolet rays absorbers such as  
benzotriazole-based ultraviolet rays absorber,  
benzophenone-based ultraviolet rays absorber, benzoate-  
based ultraviolet rays absorber, cyano acrylate-based  
5 ultraviolet rays absorber, salicylic acid-based ultraviolet  
rays absorber, hindered amine-based ultraviolet rays  
absorber and the like, epoxydized vegetable oils such as  
epoxydized soybean oil, epoxydized linseed oil, epoxydized  
rape seed oil and the like, isopropyl acid phosphate, liquid  
10 paraffin and the like. The examples of the dye stuff include  
rhodamines such as rhodamine B, solar rhodamine and the like,  
Yellow #4, Magenta #1, Cyan #2 and the like, and the examples  
of the perfume include esters such as ethyl acetoacetate,  
methyl anthranilate, isoamyl isovalerate, ethyl enanthate,  
15 ethyl cinnamate, isoamyl butyrate and the like, organic acids  
such as caproic acid, cinnamic acid and the like, alcohols  
such as cinnamate alcohol, geraniol, citral, decyl alcohol  
and the like, aldehydes such as vanillin, piperonal, peryl  
aldehyde and the like, ketones such as maltol, methyl  $\beta$ -  
20 naphthyl ketone and the like, menthols, and the like.

The examples of the thermosetting resin used in the  
present invention include polyurethane resins, epoxy resins,  
unsaturated polyester resins, phenol resins, urea-melamine  
resins, silicone resins and the like.

25 The granular pesticidal composition of the present  
invention can be obtained by coating a pesticidal active

ingredient-containing granule, for example, a conventional  
pesticidal granule, with a thermosetting resin.

As the concrete coating treatment method, there is  
usually used a method in which a monomer which can form a  
5 thermosetting resin by causing a curing reaction is added  
to the pesticidal active ingredient-containing granule under  
heating optionally in the presence of a catalyst to cause  
the curing reaction for coating.

When coating is conducted with a polyurethane resin,  
10 polyisocyanate and polyol are subjected to a curing reaction  
in the presence of a curing agent such as an organic metal,  
amine and the like. The examples of the curing agent include  
organic metals such as dibutyltin diacetate, dibutyltin  
dichloride, dibutyltin dilaurate, dibutylthio stannate, tin  
15 (I) octylate, di-n-octyltin dilaurate, isopropyl titanate,  
tetrabutyl titanate, oxyisopropyl vanadate, n-propyl  
zirconate and the like, amines such as triethylenediamine,  
N-methylmorpholine, N,N-dimethyldidodecylamine, N-  
dodecylmorpholine, N,N-dimethylcyclohexylamine, N-  
20 ethylmorpholine, dimethylethanolamine, N,N-  
dimethylbenzylamine, 1,8-diazabicyclo[5.4.0]undeca-7-ene,  
1,4-diazabicyclo[2.2.2]octane, and the like.

When coating is conducted with an epoxy resin, a method  
in which phenol or alcohol and epichlorohydrin are subjected  
25 to a curing reaction in the presence of a curing agent, a  
method in which a carboxylic acid and epichlorohydrin are



subjected to a curing reaction in the presence of a curing agent, a method in which amine, cyanuric acid or hydantoin and epichlorohydrin are subjected to a curing reaction in the presence of a curing agent, and the like are listed. The

5 examples of the curing agent used in the present invention include diethyltri-amine, triethylenetetramine, m-xylylenediamine, isophoronediamine, 1,3-bisaminomethylcyclohexane, diaminodiphenylmethane, m-phenylenediamine, diaminodiphenylsulfone, dicyandiamide,

10 organic acid dihydrazide, polyamide-modified polyamine, ketone-modified polyamine, epoxy-modified polyamine, thiourea-modified polyamine, Mannich-modified polyamine, Michael addition-modified polyamine, dodecenyl succinic anhydride, polyazelaic anhydride, hexahydrophthalic

15 anhydride, methyltetrahydrophthalic anhydride, methylnad-ic anhydride, trimellitic anhydride, pyromellitic anhydride, benzophenonetetracarboxylic acid, tetrabromophthalic anhydride, hettic anhydride, novolak type polyphenol, polymercaptane, polyisocyanate, carboxylic acid-containing

20 polyester resin, benzyldimethylaniline, 2,4,6-trisdimethylaminomethylphenol, 2-methylimidazole, 2-ethylimidazole, 4-methylimidazole, 2-heptadecylimidazole, aromatic sulfonium salt, aromatic diazonium salt, resol type phenol resin, methylol group-containing melamine resin and

25 the like.

Further, there is also used a method in which an

aliphatic cycloepoxy compound is subjected to a curing reaction in the presence of a curing agent such as peracetic acid and the like.

The examples of the epoxy resin produced include

5 glycidyl ether type epoxy resins such as bisphenol A type, bisphenol F type, brominated bisphenol A type, hydrogenated bisphenol A type, bisphenol S type, bisphenol AF type, biphenyl type, naphthalene type, fluorene type, phenol novolak type, o-cresol novolak type, DPP novolak type,

10 trishydroxyphenylmethane type, tetraphenylolthane type and the like, glycidylamine type epoxy resins such as tetraglycidyl-diaminodiphenylmethane type, triglycidylisocyanurate type, hydantoin type, aminophenol type, aniline type, toluidine type, alicyclic epoxy resins

15 and the like.

When coating is conducted with unsaturated polyester resin, unsaturated dibasic acid or unsaturated dibasic acid anhydride and a dihydric alcohol are subjected to a curing reaction in the presence of a vinyl monomer. The examples

20 of the unsaturated dibasic acid include phthalic anhydride, isophthalic acid, terephthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrabromophthalic anhydride, tetrachlorophthalic anhydride, hettic anhydride,

25 endomethylenetetrahydrophthalic anhydride and the like, and the examples of the dihydric alcohol include ethylene glycol,

propylene glycol, 1,3-butylene glycol, 1,6-hexane diol,  
diethylene glycol, dipropylene glycol, neopentyl glycol,  
triethylene glycol, hydrogenated bisphenol A,  
bisphenoldihydroxypropyl ether and the like. The examples  
5 of the vinyl monomer include styrene, vinyltoluene,  
chlorostyrene, diallyl phthalate, triallyl cyanurate,  
methyl methacrylate and the like.

When, coating is conducted with a phenol resin, phenol  
and aldehyde are subjected to a curing reaction in the  
10 presence of a catalyst such as hydrochloric acid, oxalic acid,  
hexamethylene diamine and the like. The examples of the  
phenol herein used include phenol (in a narrow sense),  
o-cresol, m-cresol, p-cresol, xylenol, p-tert-butylphenol,  
resorcinol and the like. In this curing reaction, a novolak  
15 type phenol resin is obtained in the presence of an acidic  
catalyst, and a resol type phenol resin is obtained in the  
presence of a basic catalyst.

When coating is conducted with a urea-melamine resin,  
urea or melamine and form aldehyde are subjected to a curing  
20 reaction in the presence of a basic catalyst.

Further, when coating is conducted with a silicone resin,  
a silicone and polyfunctional siloxane are subjected to a  
curing reaction in the presence of a catalyst.

In the present invention, it is convenient to conduct  
25 coating with a polyurethane resin or epoxy resin as a  
thermosetting resin in view of easy handling of the monomer,

conditions of the curing reaction and the like. In particular, it is preferable that the pesticidal active ingredient-containing granule is coated using a solution obtained by adding catalyst(s) to respective monomers, i.e.

5 a polyisocyanate and polyol and the product is kept at a temperature from 5 to 120°C for 3 to 60 minutes for coating the pesticidal active ingredient-containing granule with a polyurethane resin, in view of handling. In this method, the polyisocyanate and polyol as monomers used for coating may

10 be composed solely of the monomer, or may be a solution or further an aqueous emulsion or organic solvent-based emulsion.

The examples of the polyisocyanate include toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI),

15 naphthalene diisocyanate, tolidine isocyanate, hexamethylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, 4,4-methylenebis(cyclohexyl isocyanate), trimethylhexamethylene diisocyanate, 1,3-(isocyanatemethyl)cyclohexane, triphenylmethane

20 triisocyanate, tris(isocyanatephenyl)thiophosphate, and a mixture thereof, and the like.

Further, instead of these polyisocyanate monomers used for coating, modified polyisocyanates and oligomeric polyisocyanates thereof can also be used. The examples of

25 the modified polyisocyanates include adduct modified polyisocyanates, biuret modified polyisocyanates,

isocyanurate modified polyisocyanates, block type polyisocyanates, prepolymer type polyisocyanates, dimerized polyisocyanates and the like.

The examples of the polyol include condensated  
5 polyester polyols, polyether polyols, polyacrylic acid polyols, lactone-based polyester polyols, polycarbonate polyols, natural polyols and modified compounds thereof, and the like. The condensated polyester polyol can usually be obtained by condensation reaction of a polyol with a dibasic  
10 acid. The polyether polyol can usually be obtained by polymerization reaction of a cyclic oxide. The polyacrylic acid polyol can usually be obtained by condensation reaction of a polyacrylic acid with a polyol, or by polymerization reaction of an acrylate monomer obtained by condensation  
15 reaction of acrylic acid with a polyol. The lactone-based polyester polyol can be obtained, for example, by ring-opening polymerization of  $\epsilon$ -caprolactam using a polyhydric alcohol as an initiator. The polycarbonate polyol can usually be obtained by reaction of a glycol with a carbonate.  
20 The examples of the polyol used to obtain a condensated polyester polyol and polyacrylic acid polyol usually include methylene glycol, ethylene glycol, propylene glycol, tetramethylene glycol, hexamethylene glycol, trimethylolpropane, polytetramethylene glycol, glycerin,  
25 pentaerythritol, sorbitol, sucrose and oligomers thereof, and the like. As the dibasic acid used to obtain a condensated

polyester polyol, adipic acid, phthalic acid or the like are usually used. Further, the above-described acrylic acid may be substituted by methacrylic acid.

In producing the granular pesticidal composition of the present invention, the method for coating the pesticidal active ingredient-containing granule with a thermosetting resin is as follows.

First, the pesticidal active ingredient-containing granule is mixed by a mixer such as a rolling pan, rolling drum and the like (preferably equipped with a heating apparatus). A monomer for thermosetting resin, or a solution, suspension, emulsion or the like thereof are added into the mixer under heating by dropping, spraying or the like.

If desired, this operation is repeated for several times (preferably 2 to 200 times). In particular, in the case wherein controlled release of the pesticidal active ingredient for a long term is required, it is necessary to increase the proportion of the thermosetting resin against the pesticidal active ingredient-containing granule. In this case, however, if a lot of monomer for thermosetting resin is added in one time to the pesticidal active ingredient-containing granule which is being rolled, an uncured thermosetting resin composition tends to have stringiness and the pesticidal active ingredient-containing granule tends to become a agglomerate. Therefore, it is

preferable to repeat several times such an operation that the monomer for thermosetting resin is added bit by bit, preferably added so that the proportion of the thermosetting resin is from 0.05 to 1.5 parts by weight in one time based  
5 on 100 parts by weight of the pesticidal active ingredient-containing granule to be coated, and the pesticidal active ingredient-containing granule is coated with the thermosetting resin by keeping heating.

In this manner, the pesticidal active ingredient-  
10 containing granule is coated with the thermosetting resin, and it is preferable that the proportion of the thermosetting resin is from 0.5 to 15 parts by weight based on 100 parts by weight of the pesticidal active ingredient-containing granule to be coated, generally in view of durability of  
15 effect of the resulting granular pesticidal composition.

Further, after the pesticidal active ingredient-containing granule is coated with the thermosetting resin, it is preferable to keep the coated granule at from 5 to 120°C for 3 to 120 minutes, preferably from 40 to 100°C for 5 to  
20 30 minutes to cure the thermosetting resin completely.

In the present invention, respective objects can be attained by increasing the proportion of the thermosetting resin against the pesticidal active ingredient-containing granule in the case where controlled release of the pesticidal  
25 active ingredient for longer period is required, and by decreasing the proportion of the thermosetting resin against

the pesticidal active ingredient-containing granule in the case where controlled release of the pesticidal active ingredient for longer period is not so required, to the contrary. In addition, extent of the controlled release can  
5 be controlled by appropriately selecting the kind of the thermosetting resin.

Namely, when crosslinking degree of the thermosetting resin is increased, for example, when a polyurethane resin is used, it is possible to accomplish controlled release of  
10 the pesticidal active ingredient for longer period by selecting polyisocyanate having tri- or higher isocyanate groups and/or polyol having tri- or higher hydroxy groups. In general, it is usually preferable to select a resin having low water absorption ratio (preferably not more than 5%) and  
15 high glass transition temperature in selecting a thermosetting resin having high crosslinking degree. Of course, it is also possible to attain controlled release of necessary extent by mixing two or more resins and appropriately selecting the mixing ratio.

20 The present invention is then more specifically described by production examples and test examples.

#### Production Example 1

Four parts by weight of N-(1,1,3-trimethyl-2-oxa-4-indanyl)-5-chloro-1,3-dimethylpyrazole-4-carboxamide  
25 [Furametpyr] and 0.8 parts by weight of hydrated silica was completely mixed in a juice mixer, and then, the mixture was



ground by a pin mill. The resulting ground material has an average particle size of 19.1  $\mu$  m (measured value by Coulter Counter TA II type).

The resulting ground material (4.8 parts by weight )  
5 obtained above, 30 parts by weight of Bentonite Fuji  
(bentonite manufactured by Hojun Yoko K.K.), 2 parts by weight  
of Cellogen 7A (sodium carboxymethylcellulose manufactured  
by Dai-ichi Kogyo Seiyaku Co., Ltd.), 0.5 parts by weight  
of sodium hexametaphosphate and 60.7 parts by weight of kaolin  
10 clay were completely mixed by a juice mixer, and the mixture  
was transferred to a mortar, and to this were added 10 parts  
by weight of 20% by weight aqueous solution of sodium  
dodecylbenzenesulfonate and 12 parts by weight of water, and  
they were completely kneaded. The resulting kneaded  
15 material was granulated by a laboratory extruding granulator  
equipped with a 1.2 mm  $\phi$  die plate, dried at 60°C for 15 minutes,  
then the particle size was made uniform, to obtain the  
pesticidal active ingredient-containing granule having a  
particle size from 1400 to 850  $\mu$  m (This pesticidal active  
20 ingredient-containing granule is also comparative granular  
pesticidal composition used for comparison in the test  
examples described below.).

One kilogram of the resulting pesticidal active  
ingredient-containing granule was rolled at 20 to 30 rpm in  
25 an inclined pan type rolling granulator which could control  
temperature equipped with a hot air generator, and to this

was added 5 g of a mixture obtained by mixing 46.5 parts by weight of a polymeric MDI (mixture having a polymerization degree of 1 to 3), 52.5 parts by weight of a trifunctional polypropylene glycol polyol and 1 part by weight of

5 2,4,6-tris(dimethylaminomethyl)phenol with maintaining the temperature at from 65 to 70°C, and the temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI, trifunctional polypropylene glycol polyol and 2,4,6-  
10 tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 18 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal composition (1) of the present invention.

15 Production Example 2

A granular pesticidal composition (2) of the present invention was produced in the same manner as in Production Example 1 except that the operation that the mixture of the polymeric MDI, trifunctional polypropylene glycol polyol and  
20 2,4,6-tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times instead of 18 times in the Production Example 1.

Test Example 1

25 Into a 500 ml beaker were charged the granular pesticidal compositions (1) and (2) obtained in Production Examples 1

and 2 and the comparative granular pesticidal composition (300 mg, respectively) and 300 ml of 3° hardness water, and the mixture was stirred mildly. The temperature of the solution was kept at  $25 \pm 1^\circ\text{C}$ , and after given time, 1ml of the solution took out from the center part of the beaker was analyzed by gas chromatography to measure the amount of the pesticidal active ingredient, and release ratio was calculated by the following formula.

$$\text{Release ratio (\%)} = \frac{\text{Amount of pesticidal active ingredient (mg) in 1 ml of sample} \times 300}{\text{Initial amount of pesticidal active ingredient (mg) in 300 mg of composition tested}} \times 100$$

10

Table 1

	Release ratio (%)		
	One day after	21 days after	42 days after
Granular pesticidal composition (1)	23	69	91
Granular pesticidal composition (2)	16	48	64
Comparative granular pesticidal composition	100	100	100

As shown in the above table, as to the comparative granular pesticidal composition, the pesticidal active ingredient is quickly eluted, while, as to the granular

15

pesticidal composition of the present invention, controlled release of the pesticidal active ingredient for long period is attained.

5 The granular pesticidal compositions (1) and (2) of the present invention containing as a pesticidal active ingredient Furametpyr which is a fungicidal compound are very effective for use for nersery box treatment of a rice plant by making the best use of the controlled release for a long time.

10 As is known from comparison between the granular pesticidal composition (1) of the present invention [the proportion of the thermosetting resin is about 9 parts by weight based on 100 parts by weight of the pesticidal active ingredient-containing granule to be coated] and the granular  
15 pesticidal composition (2) of the present invention [the proportion of the thermosetting resin is about 10 parts by weight based on 100 parts by weight of the pesticidal active ingredient-containing granule to be coated], the extent of controlled release of the pesticidal active ingredient is  
20 controlled by changing the using ratio of the thermosetting resin.

Examples in which the extent of controlled release of the pesticidal active ingredient is controlled by changing the kind of the thermosetting resin are shown below.

#### 25 Production Example 3

First, a pesticidal active ingredient-containing

granule having a particle size from 1400 to 850  $\mu$ m was obtained in the same manner as in Production Example 1.

One kilogram of the resulting pesticidal active ingredient-containing granule was rolled at 20 to 30 rpm in an inclined pan type rolling granulator which could control temperature equipped with a hot air generator, and to this was added 5 g of a mixture obtained by mixing 135 parts by weight of a polymeric MDI (mixture having a polymerization degree of 1 to 3), 486 parts by weight of a trifunctional polypropylene glycol polyol and 12 part by weight of 2,4,6-tris(dimethylaminomethyl)phenol with maintaining the temperature at from 65 to 70°C, and the temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI, trifunctional polypropylene glycol polyol and 2,4,6-tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal composition (3) of the present invention.

#### Production Example 4

First, a pesticidal active ingredient-containing granule having a particle size from 1400 to 850  $\mu$ m was obtained in the same manner as in Production Example 1.

One kilogram of the resulting pesticidal active ingredient-containing granule was rolled at 20 to 30 rpm in

an inclined pan type rolling granulator which could control temperature equipped with a hot air generator, and to this was added 5 g of a mixture obtained by mixing 45.2 parts by weight of a polymeric MDI (mixture having a polymerization  
5 degree of 1 to 3), 18.3 parts by weight of a trifunctional polypropylene glycol polyol, 36.6 parts by weight of a difunctional polypropylene glycol polyol and 2.0 parts by weight of 2,4,6-tris(dimethylaminomethyl)phenol with maintaining the temperature at from 65 to 70°C, and the  
10 temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI, trifunctional polypropylen glycol polyol, difunctional polypropylene glycol polyol and 2,4,6-tris(dimethylaminomethyl)phenol was added and the resulting  
15 mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal composition (4) of the present invention.

#### Production Example 5

20 First, a pesticidal active ingredient-containing granule having a particle size from 1400 to 850  $\mu$ m was obtained in the same manner as in Production Example 1.

One kilogram of the resulting pesticidal active ingredient-containing granule was rolled at 20 to 30 rpm in  
25 an inclined pan type rolling granulator which could control temperature equipped with a hot air generator, and to this

was added 5 g of a mixture obtained by mixing 35.8 parts by weight of a polymeric MDI (mixture having a polymerization degree of 1 to 3), 31.1 parts by weight of a trifunctional polypropylene glycol polyol, 31.1 parts by weight of a difunctional polypropylene glycol polyol and 1.5 part by weight of 2,4,6-tris(dimethylaminomethyl)phenol with maintaining the temperature at from 65 to 70°C, and the temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI, trifunctional polypropylene glycol polyol, difunctional polypropylene glycol polyol and 2,4,6-tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal composition (5) of the present invention.

#### Production Example 6

First, a pesticidal active ingredient-containing granule having a particle size from 1400 to 850  $\mu$ m was obtained in the same manner as in Production Example 1.

One kilogram of the resulting pesticidal active ingredient-containing granule was rolled at 20 to 30 rpm in an inclined pan type rolling granulator which could control temperature equipped with a hot air generator, and to this was added 5 g of a mixture obtained by mixing 40.9 parts by weight of a polymeric MDI (mixture having a polymerization

degree of 1 to 3), 39.4 parts by weight of a trifunctional polypropylene glycol polyol, 19.7 parts by weight of a difunctional polypropylene glycol polyol and 1.5 parts by weight of 2,4,6-tris(dimethylaminomethyl)phenol with

- 5 maintaining the temperature at from 65 to 70°C, and the temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI, trifunctional polypropylene glycol polyol, difunctional polypropylene glycol polyol and 2,4,6-
- 10 tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal composition (6) of the present invention.

15 Production Example 7

First, a pesticidal active ingredient-containing granule having a particle size from 1400 to 850  $\mu$ m was obtained in the same manner as in Production Example 1.

- One kilogram of the resulting pesticidal active
- 20 ingredient-containing granule was rolled at 20 to 30 rpm in an inclined pan type rolling granulator which could control temperature equipped with a hot air generator, and to this was added 5 g of a mixture obtained by mixing 135 parts by weight of a polymeric MDI (mixture having a polymerization
- 25 degree of 1 to 3), 148 parts by weight of a trifunctional polypropylene glycol polyol and 2.8 parts by weight of



2,4,6-tris(dimethylaminomethyl)phenol with maintaining the temperature at from 65 to 70°C, and the temperature of the mixture was kept at from 65 to 70°C for 4 minutes. The same operation that the mixture of the polymeric MDI,  
5 trifunctional polypropylene glycol polyol and 2,4,6-tris(dimethylaminomethyl)phenol was added and the resulting mixture was kept at from 65 to 70°C for 4 minutes was repeated 20 times, and finally, the resulting mixture was kept at from 65 to 70°C for 10 minutes to produce a granular pesticidal  
10 composition (7) of the present invention.

#### Test Example 2

Into a 500 ml beaker were charged the granular pesticidal compositions obtained in Production Examples 3 to 7 (300 mg, respectively) and 300 ml of 3° hardness water, and the mixture  
15 was stirred mildly. The temperature of the solution was kept at 25±1°C, and after given time, 1ml of the solution took out from the center part of the beaker was analyzed by gas chromatography to measure the amount of the pesticidal active ingredient therein, and release ratio was calculated  
20 appropriately by the following formula.

$$\text{Release ratio (\%)} = \frac{\begin{array}{l} \text{Amount of pesticidal active} \\ \text{ingredient (mg) in 1 ml of sample} \\ \times 300 \end{array}}{\begin{array}{l} \text{Initial amount of pesticidal} \\ \text{active ingredient (mg) in 300 mg} \\ \text{of composition tested} \end{array}} \times 100$$

And, number of days required for 50% release of the pesticidal active ingredient was calculated by interpolation method. The results are shown in Table 2.

In the table, polyol equivalent (OH equivalent) of the thermosetting resin used for coating, Tg (value read from peak of dissipation elasticity modulus obtained in viscoelasticity measurement) and water absorption ratio (%) after kept in boiling water for 24 hours are also described.

10

Table 2

	Number of days for 50% release (day)	OH equivalent	Tg (°C)	Water absorption ratio
Granular pesticidal composition (3)	3	486	-24	6.19
Granular pesticidal composition (4)	5	279	15	3.64
Granular pesticidal composition (5)	9	230	28	3.32
Granular pesticidal composition (6)	14	196	57	2.97
Granular pesticidal composition (7)	25	148	73	2.17

As shown in the above table, extent of controlled release tends to increase when OH equivalent of a thermosetting resin becomes lower (water absorption ratio becomes lower), and therefore, controlled release of the pesticidal active ingredient corresponding to the object can be conducted by appropriately changing the kind and amount of a thermosetting resin depending on use occasion.

### Effect of the Invention

According to the present invention, release of the  
pesticidal active ingredient can be controlled, and  
5 controlled release of the pesticidal active ingredient can  
be accomplished.

What is claimed is:

1. A granular pesticidal composition coated with a thermosetting resin.

5        2. The granular pesticidal composition according to Claim 1, wherein the thermosetting resin is a polyurethane resin.

3. The granular pesticidal composition according to Claim 1 or 2, wherein the proportion of the thermosetting  
10 resin is from 0.5 to 15 parts by weight based on 100 parts by weight of a pesticidal active ingredient-containing granule to be coated.

4. A granular pesticidal composition according to claim 2 or 3, wherein the thermosetting resin is prepared from  
15 polyisocyanate having tri- or higher isocyanate groups and/or polyol having tri- or higher hydroxy groups.

5. A granular pesticidal composition according to any one of claims 1 to 4, wherein the water absorption ratio of the thermosetting resin is not more than 5%.

20        6. The manufacturing method of the granular pesticidal composition according to any one of claims 1 to 5, comprising repeating the operation that 0.05 to 1.5 parts by weight of a monomer for preparing the thermosetting resin is added to  
25 100 parts by weight of the pesticidal active ingredient-containing granule to be coated in one time.

## Abstract

This invention relates to a granular pesticidal composition coated with a thermosetting resin.

5       Release of the pesticidal active ingredient in the granular pesticidal composition of the present invention is suitably controlled by appropriately changing the kind and amount of a thermosetting resin depending on use occasion, and durability of effect of the pesticidal active ingredient  
10   is obtained.